```
     FILE 'REGISTRY' ENTERED AT 23:18:24 ON 10 MAR 2002
L1             2 S TITANIUM OXIDE/CN

     FILE 'MEDLINE, BIOSIS, CA, CAPLUS, CAOLD, EMBASE, USPATFULL, PROMT'
     ENTERED AT 23:18:59 ON 10 MAR 2002
L2        291172 S L1 OR TITANIUM OXIDE
L3         18218 S PHOTOCATALYTIC
L4         10657 S L2 AND L3
L5          5372 S L3 (S) L2
L6       2783957 S PLAQUE OR BIOFILM OR DENTAL OR CARIES OR FILM OR HALITOSIS
L7          1015 S L5 AND L6
L8       1570875 S SILICON
L9           135 S L7 AND L8
L10          108 DUP REM L9 (27 DUPLICATES REMOVED)
L11       408979 S TEETH OR TOOTH
L12            2 S L10 AND L11
L13            6 S L5 AND L11
L14            5 DUP REM L13 (1 DUPLICATE REMOVED)
L15          275 S L5 AND L8
L16          184 DUP REM L15 (91 DUPLICATES REMOVED)
L17          108 S L16 AND L6

     FILE 'STNGUIDE' ENTERED AT 23:31:21 ON 10 MAR 2002

     FILE 'MEDLINE, CA, USPATFULL' ENTERED AT 23:36:18 ON 10 MAR 2002

     FILE 'STNGUIDE' ENTERED AT 23:36:18 ON 10 MAR 2002

     FILE 'MEDLINE, CA, USPATFULL' ENTERED AT 23:38:09 ON 10 MAR 2002

     FILE 'STNGUIDE' ENTERED AT 23:38:09 ON 10 MAR 2002
L18            0 S ALCOHOL OR ACETONE OR METHYL ETHYL KETONE OR ETHYL ACETATE
OR

     FILE 'MEDLINE, BIOSIS, CA, CAPLUS, CAOLD, EMBASE, USPATFULL, PROMT'
     ENTERED AT 23:42:01 ON 10 MAR 2002
L19      1920702 S ALCOHOL OR ACETONE OR METHYL ETHYL KETONE OR ETHYL ACETATE
OR

=> s l17 and l19
L20           61 L17 AND L19

=> s oral or dent?
L21      1947662 ORAL OR DENT?

=> s l20 and l21
L22            5 L20 AND L21

=> d l22 bib, ab, kwic

L22  ANSWER 1 OF 5  USPATFULL
AN     2002:48097  USPATFULL
TI     Long lasting coatings for modifying hard surfaces and processes for
       applying the same
IN     Rohrbaugh, Robert Henry, Hamilton, OH, UNITED STATES
       Goldstein, Alan Scott, Blue Ash, OH, UNITED STATES
       McDonald, Michael Ray, Middletown, OH, UNITED STATES
       O'Connor, Helen Frances, Loveland, OH, UNITED STATES
       Liddle, Heather Anne, Cincinnati, OH, UNITED STATES
```

Jensen, John Michael, Wyoming, OH, UNITED STATES
Sakkab, Nabil Yaqub, Cincinnati, OH, UNITED STATES
PA The Procter & Gamble Company (non-U.S. corporation)
PI US 2002028288 A1 20020307
AI US 2001-828014 A1 20010406 (9)
PRAI WO 2000-US16349 20000614
US 2001-265059 20010130 (60)
DT Utility
FS APPLICATION
LREP THE PROCTER & GAMBLE COMPANY, PATENT DIVISION, IVORYDALE TECHNICAL CENTER - BOX 474, 5299 SPRING GROVE AVENUE, CINCINNATI, OH, 45217
CLMN Number of Claims: 38
ECL Exemplary Claim: 1
DRWN 2 Drawing Page(s)
LN.CNT 3227
AB Materials for coating, coating compositions, methods and articles of manufacture comprising a nanoparticle system or employing the same to impart surface modifying benefits for all types of inanimate hard surfaces are disclosed. In some embodiments, dispersement of nanoparticles in a suitable carrier medium allows for the creation of coating compositions, methods and articles of manufacture that create multi-use benefits to modified hard surfaces. These surface modifications can produce long lasting or semi-permanent multi-use benefits that include at least one of the following improved surface properties: wetting and sheeting, quick drying, uniform drying, soil removal, self-cleaning, anti-spotting, anti-soil deposition, cleaner appearance, enhanced gloss, enhanced color, minor surface defect repair, smoothness, anti-hazing, modification of surface friction, release of actives and transparency, relative to hard surfaces unmodified with such nanoparticle systems. Actively curing the coating composition on the hard surfaces, including, but not limited to by radiative heating the air surrounding the hard surface with the coating thereon can be used to increase the durability of the hard surface coating.
SUMM [0005] The current approach to solving the coating problem is with the use of surfactants, **film**-forming polymer coatings, clay-containing-**film**-forming polymer coatings and photoactive inorganic metal oxide coatings. However, the substantivity of the **film**-forming polymers (e.g. alkoxylated silicones, poly(N-vinyl-2-pyrrolidones, poly(N-vinyl-imidazoles, diblock copolymers of poly(ethylene oxide) and poly(lactide)) is poor such that its wetting/sheeting effect. . . . exteriors, shower units and dishware where elevated levels of polymers result in unacceptable residue problem. In the case of clay-containing, **film**-forming polymer coatings, the nanoparticles are rheology agents for the formulations and do not themselves impart the benefit disclosed. One example. . .
SUMM . . . clay in a non-enzymatic dish-washing composition with a reduced pH of 9-11 to provide for a reduction of spot and **film** formation on the cleaned articles. See also U.S. Pat. No. 4,591,449. EP. Pat. No. 139,330 B1, titled "Rinse Aid" discloses. . . layered clay is introduced in the machine dishwashing detergent or rinse aide as a single-use application to prevent spotting and **film** formation during that particular wash cycle. These patents do not disclose a nanoparticle coating system requirement which is preventative in. . .

SUMM . . . in JP. Pat. No. 11181339 A2, titled "Hydrophilic Coating Composition", discloses a room-temperature-settable coating composition comprising an aqueous fluid containing **photocatalytic titanium oxide** particles having a particle diameter of 1-100 nm and tin oxide particles having a particle diameter of 1-100 nm and having a pH of 8-12 or a pH of 0-5, and a coating **film** which exhibits hydrophilicity when it is formed on a substrate and irradiated with ultraviolet rays at a wavelength of 200-400 nm and, and the **photocatalytic titanium oxide** is photoexcited. Other related patents disclosing methods and articles of use for the abovementioned **titanium oxide** coating composition include JP. Pat. No. 11172239 A2, titled "Hydrophilic Member, Method For Hydrophilization/Hydrophilicity Retention Of Surface Of Member, And. . . And Its Anti-Fogging Method"; and JP. Pat. No. 09228072 A2, titled "Outdoor Member". In the abovementioned patents, the hydrophilic TiO.sub.2 **film** can cause photo- and chemical-degradation of organic undercoats, and any rubber or plastic it comes into contact with, and requires. . .

SUMM . . . Divided Hydrophobic Oxide Particles" discloses a process for preparing hydrophobic finely divided particles of oxides of metals and/or oxides of **silicon** by chemically bonding hydrocarbon radicals to the surface of the oxide particles.

SUMM . . . in U.S. Pat. No. 4,173,480, titled "Photographic Sheet With Synthetic Hectorite Antistatic Additive As Sizing Or Backcoat", wherein a polymer **film** base is coated with a synthetic hectorite clay, specifically Laponite S.TM.. The binder is gelatin, starch or carboxy methylcellulose. The. . .

SUMM [0013] Another example is disclosed in JP. Pat. No. 8053558 A2, titled "Anti-Fog Synthetic Resin **Film** For Agriculture", wherein colloidal alumina, colloidal silica, anionic surfactant, organic electrolyte and an inorganic layered compound form a **film** that exhibits sustained anti-fog properties at low- and high-temperatures. Another example is disclosed in JP. Pat. No. 04353438 A2, titled. . . the films useful for greenhouses, book covers, card holders, etc.. See also, EP 0732387 titled, "Antifogging agent composition and agricultural **film** coated therewith".

SUMM [0014] Another example is disclosed in U.S. Pat. No. 4,786,558, titled "Composite **Film** And Antistatic Composite **Film** Comprising A Swellable Inorganic Silicate", where the inorganic nanoparticle is modified by treating it with various ions to provide a composite **film** with antistatic benefits comprising a swellable inorganic silicate.

DETD . . . example, by grinding as described in EP-A 637,616 or by dispersion in a suitable carrier medium, such as water or water/**alcohol** and mixtures thereof.

DETD . . . section at the end of this description. Examples of other suitable dispersants include, but are not limited to: poly (acrylic/allyl **alcohol**), poly (acrylic/maleic), poly (a-hydroxyacrylic acid), poly (tetramathylene-1,2-dicarbocylic acid), poly (4-methocy-tetramethylene-1,2-dicarbocylic acid) -sodium tripolyphosphate, pyrophosphate, and the other dispersants and builders.

. .

DETD . . . 99.99%, alternatively from about 80% to about 99.99%, by weight of liquid carrier or suitable carrier medium, such as an **alcohol** and/or water.

DETD . . . make the nanoparticle on which the polymer is adsorbed hydrophobic; polyvinyl acetate with sufficient hydrolysis to provide hydrophilicity; and polyvinyl **alcohol** and hydrophobically modified polyvinyl **alcohol**, provided that the level of hydrophobe is not sufficient to render the nanoparticle on which the polymer is adsorbed hydrophobic.

DETD [0149] straight-chain, primary **alcohol** ethoxylates, with R being C.sub.8-C.sub.18 alkyl and/or alkenyl group, alternatively CIO-C.sub.14, and s being from about 2 to about 8;

DETD [0150] straight-chain, secondary **alcohol** ethoxylates, with R being C.sub.8-C.sub.18 alkyl and/or alkenyl, e.g., 3-hexadecyl, 2-octadecyl, 4-eicosanyl, and 5-eicosanyl, and s being from about 2. . .

DETD [0152] branched chain **alcohol** ethoxylates, wherein branched chain primary and secondary alcohols (or Guerbet alcohols), which are available, e.g., from the well-known "OXO" process. . .

DETD [0153] Other examples of alternative ethoxylated surfactants include carboxylated **alcohol** ethoxylate, also known as ether carboxylate, with R.sup.8 having from about 12 to about 16 carbon atoms and s being. . .

DETD . . . acid and potassium sorbate. Nonlimiting examples of useful nonionic antimicrobials/preservatives which are potentiated by aminocarboxylate chelators are DMDM hydantoin, phenethyl **alcohol**, monolaurin, imidazolidinyl urea, and Bronopol (2-bromo-2-nitropropane-1,3-diol).

DETD [0223] Alicyclic and heterocyclic polycarboxylates include cyclopentane-cis,cis,cis-tetracarboxylates, cyclopentadienide pentacarboxylates, 2,3,4,5-tetrahydro-furan-cis, cis, cis-tetracarboxylates, 2,5-tetrahydro-furan -cis-dicarboxylates, 2,2,5,5-tetrahydrofuran-tetracarboxylates, 1,2,3,4,5,6-**hexane** -hexacarboxylates and carboxymethyl derivatives of polyhydric alcohols such as sorbitol, mannitol and xylitol. Aromatic poly-carboxylates include mellitic acid, pyromellitic acid. . .

DETD . . . desirable to modify the application procedure. For instance, the clearcoat composition could first be applied, and then a "skim" or **film** could be formed on the top of the wet clear coat using techniques known to those of skill in the. . .

DETD . . . does not exclude the weathering or optionally the normal use of the surface. Not to be limited by theory, the strippable-**film** mechanism of this method is depicted in FIGS. 1-3.

DETD . . . invention, such as an automotive, exterior building or dishware surface application, an effective nanoparticle coating is deposited as an invisible **film**, preventing soil 26 from adhering to the hard surface 20 (FIG. 1). The nanoparticle coating consists of multiple effective layers. . .

DETD . . . a sheet either attached to the container or accompanying it when purchased; or in advertisements, demonstrations, and/or other written or **oral** instructions which may be connected to the purchase or use of the coating compositions.

DETD . . . hard surfaces are as follows:

TABLE 5

	% by weight	
Component	28	29
1. Nanoclay	0.005-2	0.005-2

2. Ether capped poly(oxyalkylated) **alcohol** -- 0.01-1
3. Water Balance Balance

1. Nanoclay can be any of the available synthetic hectorite clays, such as Laponite RD .TM. or B .TM. from Southern Clay Products, Inc.
2. Ether capped poly (oxyalkylated) **alcohol** acts as a nonionic wetting agent.
3. Water is used for balance.

DETD . . . in an oven for 30 min. at 265.degree. F. (129 .degree. C.) (this temperature is the substrate, or panel, temperature). **Film** build range=0.9-1.1 mils (22.9 to 27.9 .mu.m). Once the primer has cooled, the basecoat is applied in two coats with 60 sec. flash between coats, for a **film** build of 0.6-0.8 mils (15.2 to 20.3 .mu.m). Basecoat is flashed for 2 min. before the URECLEAR .RTM. clearcoat is applied in two coats with 60 sec. flash between coats, to a **film** build of 1.9-2.1 mils (48.3 to 53.3 .mu.m). The hard surface coating can be applied to the panels at any. . .

DETD . . . horizontal, and the panel is judged to determine whether it exhibits sheeting, curtaining, or beading. "Sheeting" is when an even **film** of water covers the substrate, and slowly dries down without developing breaks in the **film**. "Curtaining" occurs when the water slowly pulls into the middle and drains off the substrate. Performance is judged to be. . .

=> file home

COST IN U.S. DOLLARS	SINCE FILE ENTRY	TOTAL SESSION
FULL ESTIMATED COST	64.48	164.96
DISCOUNT AMOUNTS (FOR QUALIFYING ACCOUNTS)	SINCE FILE ENTRY	TOTAL SESSION
CA SUBSCRIBER PRICE	0.00	-1.18

FILE 'HOME' ENTERED AT 23:45:00 ON 10 MAR 2002

=> d l22 2-5 bib, ab, kwic
YOU HAVE REQUESTED DATA FROM FILE 'USPATFULL' - CONTINUE? (Y)/N:y

L22 ANSWER 2 OF 5 USPATFULL
AN 2001:90849 USPATFULL
TI **Dental** and oralogic composition
IN Masuhara, Eiichi, Tokyo-to, Japan
Kadoma, Yoshinori, Tokyo-to, Japan
Yamauchi, Junichi, Osaka-fu, Japan
Okada, Koichi, Okayama-ken, Japan
Yamaguchi, Satoshi, Osaka-fu, Japan
PA Kuraray Co., Ltd, Kurashiki-shi, Japan (non-U.S. corporation)
PI US 2001002994 A1 20010607
AI US 2000-728121 A1 20001204 (9)
PRAI JP 1999-344938 19991203
DT Utility
FS APPLICATION
LREP OBLON SPIVAK MCCLELLAND MAIER & NEUSTADT PC, FOURTH FLOOR, 1755 JEFFERSON DAVIS HIGHWAY, ARLINGTON, VA, 22202
CLMN Number of Claims: 24
ECL Exemplary Claim: 1

DRWN No Drawings
LN.CNT 1307
CAS INDEXING IS AVAILABLE FOR THIS PATENT.
AB The first embodiment of present invention provides a composition, which includes:

(a) a **photocatalytic titanium oxide** or a **photocatalytic titanium oxide** precursor;

(b) at least one selected from the group including:

a **silicon** compound having the following formula (I):
##STR1##

wherein X.sup.1, X.sup.2, X.sup.3 and X.sup.4 each independently represent an alkoxy group or a halogen atom,

a hydrolyzate of the **silicon** compound (I), a silicone resin, silicone resin precursor and silica; and

(c) a liquid medium. Another embodiment of the present invention provides a **dental** and oralogic composition, that includes a **photocatalytic titanium oxide** or a **photocatalytic titanium oxide** precursor. Another embodiment of the present invention provides a **dental** and oralogic composition, that includes a **photocatalytic titanium oxide** or a **photocatalytic titanium oxide** precursor, and a liquid medium. The composition of the present invention is particularly suitable in **dental** and **oral** care, and other embodiments of the present invention provide methods of making and using the above-described compositions.

TI **Dental** and oralogic composition

AB (a) a **photocatalytic titanium oxide** or a **photocatalytic titanium oxide** precursor;
AB a **silicon** compound having the following formula (I):
##STR1##
AB a hydrolyzate of the **silicon** compound (I), a silicone resin, silicone resin precursor and silica; and
AB (c) a liquid medium. Another embodiment of the present invention provides a **dental** and oralogic composition, that includes a **photocatalytic titanium oxide** or a **photocatalytic titanium oxide** precursor. Another embodiment of the present invention provides a **dental** and oralogic composition, that includes a **photocatalytic titanium oxide** or a **photocatalytic titanium oxide** precursor, and a liquid medium. The composition of the present invention is particularly suitable in **dental** and **oral** care, and other embodiments of the present invention provide methods of making and using the above-described compositions.

SUMM [0002] The present invention relates to a **dental** and oralogic composition containing a **photocatalytic titanium oxide**, and to a method of forming a **photocatalytic titanium oxide**-containing **film** on the surface of a **dental** material in or not in the mouth. More preferably, the invention relates to a **dental** and oralogic composition containing a **photocatalytic titanium oxide**, which is to be applied to **dental** materials including tooth crown restorative materials, **dentures**,

denture bases, **denture** rebases, orthodontic bases, wires, bridges, mouth pieces, etc., to teeth, gums or **oral** mucous membranes, or to teeth having been restored with composite resin or coated with **dental** manicure, to thereby form a **film** of the composition on their surfaces. The **film** thus formed prevents the formation of **biofilm**, that is, **dental plaque** containing a large number of bacteria in the mouth, and prevents **dental caries** and periodontitis or prevents the promotion of such **dental** diseases. In addition, it prevents or retards the discoloration of teeth and **dental** materials to be caused by adhesion of cigarette tar or food deposits thereto, bleaches discolored teeth, and even prevents **halitosis** . The invention also relates to a method of forming such a **photocatalytic titanium oxide**-containing **film** on the surface of a **dental** material in or not in the mouth.

SUMM [0004] **Oral** diseases include **dental caries** , gingivitis, periodontitis and other periodontal diseases (pyorrhea alveolaris, etc.), stomatitis, etc. Of these, **dental caries** is one typical disease of teeth, and it is believed to be caused by intrabuccal microorganisms that produce acid, which dissolves the enamel of teeth. Above all, it is said that Streptococcus mutans is a typical pathogen that causes **dental caries**. It is also said that periodontitis, which is a disease of peridentium, is caused by intrabuccal bacteria. In order to prevent and cure such diseases, it is important to immediately remove the **dental plaque** of intrabuccal bacteria adhered to the surface of teeth.

SUMM [0005] Expectant treatment has heretofore been employed to prevent and cure for each of the above types of **oral** diseases. For example, to prevent **dental caries**, fluorine-containing compounds are applied to teeth, or antibacterial agents are incorporated into **dental** materials. At present, however, these are not always effective or satisfactory in **dental** treatment. To restore and treat decayed teeth, **dental** materials such as **dental** metal (metal inlay), **dental** resin (cement for **dental** use), **dental** porcelain (porcelain inlay), composite resin (composite plastics for **dental** use) and others are used with which decayed teeth are restored or prosthetically treated. However, it is said that **dental plaque** of bacteria is readily formed on the surf aces of these **dental** materials. On the other hand, tooth brushing, mechanical **dental** scaling, and local application of chemicals to teeth and therearound have heretofore been recommended for preventing and curing periodontitis and. . . are troublesome and time-consuming, and it is difficult to say that their effect is satisfactory for preventing and curing the **dental** diseases.

SUMM [0006] The surfaces of teeth and **dental** materials are often discolored due to the adhesion of cigarette tar or food deposits thereto, but no one knows an. . . the discoloration and for removing the adhered cigarette tar or food deposits, and a solution to these problems is desirable. **Oral** diseases such as **dental caries**, gingivitis, periodontitis and other periodontal diseases (pyorrhea alveolaris, etc.) cause **halitosis**, and it is likewise desirable to establish an effective means for preventing and removing **halitosis**.

SUMM [0007] Recently, a coating material that contains a **photocatalytic titanium oxide** has been proposed. This coating material is applied to the surfaces of appliances, tiles glass articles and others to form thereon an antibacterial, antifogging, antisoiling or deodorizing **film**

owing to the **photocatalytic** activity of the **titanium oxide** in the material.

SUMM [0008] A liquid coating composition for teeth is known for applying such a **photocatalytic titanium oxide** to **dental** materials, which composition is prepared by mixing a **photocatalytic titanium oxide** with methyl .alpha.-cyanoacrylate and a resin component such as polymethyl methacrylate or the like (JP-A-175923/1997.) The published specification discloses that **dental caries** can be prevented by coating teeth with the coating composition. However, methyl .alpha.-cyanoacrylate used in the coating composition is extremely. . . and the coating composition is handled only with difficulty. In addition, the coating composition may not be completely safe for **dental** use in the mouth, since the composition contains methyl .alpha.-cyanoacrylate. Another problem with the coating composition is that its adhesion durability to teeth is poor, and the **film** that results from the coating composition is often peeled from teeth.

SUMM [0009] Accordingly, one object of the present invention is to provide a **dental** and oralogic composition, which is effective for preventing the adhesion of **dental plaque** onto the surfaces of teeth.

SUMM [0010] Another object of the present invention is to provide a **dental** and oralogic composition, which is effective for preventing the adhesion of **dental plaque** onto the surfaces of **dental** materials in the mouth and gums.

SUMM [0011] Another object of the present invention is to provide a **dental** and oralogic composition, which promotes the destruction and removal of **dental plaque** that has adhered to the surfaces of teeth and/or of **dental** materials in the mouth and gums.

SUMM [0012] Another object of the present invention is to provide a **dental** and oralogic composition, which effectively prevents and/or cures **oral** diseases and **dental** diseases such as **dental caries**, gingivitis, periodontitis and other peridental diseases (pyorrhea alveolaris, etc.), stomatitis, etc.

SUMM [0013] Another object of the present invention is to provide a **dental** and oralogic composition, which is easily handled and is highly safe.

SUMM [0014] Another object of the invention is to provide a **dental** and oralogic composition, which is effective for preventing and/or retarding the discoloration of teeth and **dental** materials caused by the adhesion of cigarette tar and/or food deposits thereto.

SUMM [0015] Another object of the invention is to provide a **dental** and oralogic composition, which is effective for bleaching discolored teeth.

SUMM [0016] Another object of the invention is to provide a **dental** and oralogic composition, which is effective for preventing and/or treating or removing **halitosis**.

SUMM [0017] Another object of the invention is to provide a method for forming a **film** that is effective for preventing and/or treating or removing **halitosis**.

SUMM [0018] Another object of the invention is to provide a method for forming a **film** that is effective for preventing and/or curing the **dental** diseases such as those mentioned above.

SUMM [0019] Another object of the invention is to provide a method for forming a **film** that is effective for preventing and/or retarding the discoloration of **dental** materials.

SUMM [0020] Another object of the invention is to provide a method for

forming a **film** that is effective for bleaching discolored teeth.

SUMM [0021] Another object of the invention is to provide a method for forming a **film** on **dental** materials not in the mouth that is effective for preventing and/or curing the **dental** diseases such as those mentioned above.

SUMM [0022] Another object of the invention is to provide a method for forming a **film** on **dental** materials not in the mouth that is effective for preventing and/or retarding the discoloration of **dental** materials.

SUMM [0023] Another object of the invention is to provide a method for forming a **film** on **dental** materials not in the mouth that is effective for bleaching discolored teeth.

SUMM [0024] Another object of the invention is to provide a method for forming a **film** on **dental** materials not in the mouth that is effective for preventing and/or treating or removing **halitosis**.

SUMM [0026] (a) a **photocatalytic titanium oxide** or a **photocatalytic titanium oxide** precursor;

SUMM [0028] a **silicon** compound having the following formula (I): ##STR2##

SUMM [0030] a hydrolyzate of the **silicon** compound (I), a silicone resin, silicone resin precursor and silica; and

SUMM [0032] Another embodiment of the present invention provides a **dental** and oralogic composition, that includes a **photocatalytic titanium oxide** or a **photocatalytic titanium oxide** precursor.

SUMM [0033] Another embodiment of the present invention provides a **dental** and oralogic composition, that includes a **photocatalytic titanium oxide** or a **photocatalytic titanium oxide** precursor, and a liquid medium.

SUMM [0034] Another embodiment of the present invention provides a **film**, which includes any of the above-described compositions.

SUMM [0035] Another embodiment of the present invention provides a method for making a **film**, that includes applying any of the above-described compositions to a surface of at least one selected from the group including teeth, gums, **dental** materials fitted in the mouth, **oral** mucous membranes, **dental** materials not in the mouth, and combinations thereof.

SUMM [0036] Another embodiment of the present invention provides a method for preventing or curing **oral** diseases or **dental** diseases, which includes:

SUMM . . . applying any of the above-described compositions to a surface of at least one selected from the group including teeth, gums, **dental** materials fitted in the mouth, **oral** mucous membranes, **dental** materials not in the mouth, and combinations thereof, to form an applied composition;

SUMM [0038] drying the applied composition to form a **photocatalytic titanium oxide**-containing **film** on the surface; and

SUMM [0039] exposing the **film** to light.

SUMM [0040] Another embodiment of the present invention provides a method for preventing or removing **halitosis**, which includes:

SUMM . . . applying any of the above-described compositions to a surface of at least one selected from the group including teeth, gums,

dental materials fitted in the mouth, **oral** mucous membranes, **dental** materials not in the mouth, and combinations thereof, to form an applied composition;

SUMM [0042] drying the applied composition to form a **photocatalytic titanium oxide**-containing **film** on the surface; and

SUMM [0043] exposing the **film** to light.

SUMM [0044] Another embodiment of the present invention provides a method for preventing or retarding the discoloration of teeth or **dental** materials, which includes:

SUMM . . . applying any of the above-described compositions to a surface of at least one selected from the group including teeth, gums, **dental** materials fitted in the mouth, **oral** mucous membranes, **dental** materials not in the mouth, and combinations thereof, to form an applied composition;

SUMM [0046] drying the applied composition to form a **photocatalytic titanium oxide**-containing **film** on the surface; and

SUMM [0047] exposing the **film** to light.

SUMM . . . applying any of the above-described compositions to a surface of at least one selected from the group including teeth, gums, **dental** materials fitted in the mouth, **oral** mucous membranes, **dental** materials not in the mouth, and combinations thereof, to form an applied composition;

SUMM [0050] drying the applied composition to form a **photocatalytic titanium oxide**-containing **film** on the surface; and

SUMM [0051] exposing the **film** to light.

SUMM [0052] Another embodiment of the present invention provides a method for treating **dental** materials, which includes:

SUMM [0053] applying any of the above-described compositions to a surface of a **dental** material, to form an applied composition;

SUMM [0054] drying or baking or drying and baking the applied composition to form a **photocatalytic titanium oxide** -containing **film** on the surface; and

SUMM [0055] exposing the **film** to light.

SUMM [0056] Another embodiment of the present invention provides a method for producing a **dental** and oralogic composition, which includes admixing a **photocatalytic titanium oxide** or a **photocatalytic titanium oxide** precursor with the **dental** and oralogic composition.

SUMM [0057] Another embodiment of the present invention provides a **film**, produced by a process that includes:

SUMM [0059] drying or baking or drying and baking the applied composition to form a **photocatalytic titanium oxide** -containing **film** on the surface.

SUMM [0060] Another embodiment of the present invention provides an article, which includes a surface and the above-described **film** in contact with the surface.

SUMM [0061] Another embodiment of the present invention provides a method for preparing a **dental** and oralogic composition, which includes admixing:

SUMM [0062] (a) a **photocatalytic titanium oxide** or a **photocatalytic titanium oxide** precursor;

SUMM [0064] a **silicon** compound having the following formula (I):

##STR3##

SUMM [0066] a hydrolyzate of the **silicon** compound (I), a silicone resin, silicone resin precursor and silica; and

SUMM [0069] The present inventors have continued to study the applicability of **photocatalytic titanium oxide** to **dental** use. The present inventors have found that a resin composition containing a **photocatalytic** anatase-type titanium dioxide, a (meth)acrylate monomer and a polymerization initiator is favorable to **dental** materials, and that, when the resin composite on is used in producing **dental** materials for **dentures**, **denture** rebases, orthodontic bases, **denture** restorative materials, mouth pieces, etc., or when it is applied to the surfaces of such **dental** materials and then exposed to light, then the smelly component having adsorbed or adhered to the **dental** materials in the mouth is decomposed to be odorless, and have already filed a patent application for the invention based. . .

SUMM [0070] The inventors have further studied, and, as a result, have found that a composition containing a **photocatalytic titanium oxide** or its precursor, at least one selected from a **silicon** compound such as an alkyl silicate or its hydrolyzed condensate, a silicone resin, a silicone resin precursor and silica, and a liquid medium is easily handleable and highly safe and has good **film**-forming ability on the surfaces of teeth and **dental** materials, like the **dental** resin composition disclosed in the above-mentioned JP-A-273412/1998, and that, when the composition is applied to the surfaces of teeth, **dental** materials or gums to form a **film** thereon and thereafter the thus-formed **film** is exposed to light, then the **film** acts to prevent the adhesion of **dental plaque** to the **film**-coated surfaces and to promote the destruction and removal of the **dental plaque** having adhered to the surfaces, thereby effectively preventing and curing **oral** diseases and **dental** diseases such as **dental caries**, gingivitis, periodontitis and other peridental diseases (pyorrhea alveolaris, etc.), stomatitis, etc.

SUMM [0071] In addition, the present inventors have found that a composition containing a **photocatalytic titanium oxide** and a liquid medium is also effective for preventing and curing such **oral** diseases and **dental** diseases, like the composition as above, and that, after the treatment with the composition for preventing and curing the diseases. . . be readily removed from the treated site through washing with water. Moreover, we have found that a composition containing a **photocatalytic titanium oxide** precursor and a liquid medium is also effective like the compositions mentioned above.

SUMM . . . present inventors have also found that the above-mentioned compositions are effective for preventing and retarding the discoloration of teeth and **dental** materials to be caused by adhesion of cigarette tar and food deposits thereto, for bleaching discolored teeth, and for preventing and removing **halitosis**.

SUMM [0073] When any of the above-mentioned compositions is applied to the surfaces of **dental** materials not in the mouth, or when a **photocatalytic titanium oxide** sol or a **photocatalytic titanium oxide** precursor is applied thereto not in the mouth, and thereafter dried and/or baked, then a **film** containing **photocatalytic titanium oxide** and having the above-mentioned effects

can be smoothly formed on the surfaces.

SUMM [0075] (1) A **dental** and oralogic composition containing;

SUMM [0076] (a) a **photocatalytic titanium oxide** or a **photocatalytic titanium oxide** precursor,

SUMM [0077] (b) at least one selected from a **silicon** compound of the following general formula (I): ##STR4##

SUMM [0078] wherein X.sup.1, X.sup.2, X.sup.3 and X.sup.4 each independently represent an alkoxy group or a halogen atom, hydrolyzate of the **silicon** compound (I), a silicone resin, silicone resin precursor and silica, and

SUMM [0080] (2) The **dental** and oralogic composition of above (1), wherein the ratio of the **photocatalytic titanium oxide** or **photocatalytic titanium oxide** precursor to at least one selected from the **silicon** compound (I), a hydrolyzate of the **silicon** compound (I), a silicone resin, a silicone resin precursor and silica falls between 20/1 and 1/100 in terms of the molar ratio of titanium atom/**silicon** atom.

SUMM [0081] (3) The **dental** and oralogic composition of above (1) or (2), wherein the **photocatalytic titanium oxide** precursor is a titanium alkoxide, and the silicone resin precursor is a silane compound and/or a silazane.

SUMM [0082] (4) A **dental** and oralogic composition containing a **photocatalytic titanium oxide** or a **photocatalytic titanium oxide** precursor.

SUMM [0083] (5) A **dental** and oralogic composition containing a **photocatalytic titanium oxide** or a **photocatalytic titanium oxide** precursor, and a liquid medium.

SUMM [0084] (6) The **dental** and oralogic composition of any of above (1) to (5), wherein the liquid medium is water, or a mixture of water and **alcohol**.

SUMM [0085] (7) The **dental** and oralogic composition of any of above (1) to (6), which contains a thickener.

SUMM [0086] (8) The **dental** and oralogic composition of any of above (1) to (7), which contains at least one of fine particles of a. . .

SUMM [0087] (9) The **dental** and oralogic composition of any of above (1) to (8) , which is to form a **film** on the surfaces of teeth, gums, **dental** materials fitted in the mouth, and/or **oral** mucous membranes, or to form a **film** on the surf aces of **dental** materials not in the mouth.

SUMM [0088] (10) A method for preventing and curing **oral** diseases and **dental** diseases, which comprises applying the **dental** and oralogic composition of any one of above (1) to (8) to the surfaces of teeth, gums, **dental** materials fitted in the mouth, and/or **oral** mucous membranes, then drying it to form a **photocatalytic titanium oxide**-containing **film** on the surf aces, and thereafter exposing the **film** to light.

SUMM [0089] (11) A method for preventing and removing **halitosis**, which comprises applying the **dental** and oralogic composition of any one of above (1) to (8) to the surf aces of teeth, gums, **dental** materials fitted in the mouth, and/or **oral** mucous membranes, then drying it to form a **photocatalytic titanium oxide**-containing **film** on the surf aces, and thereafter exposing the **film** to light.

SUMM [0090] (12) A method for preventing and retarding the discoloration of teeth and **dental** materials, which comprises applying the **dental** and oralogic composition of any one of above (1) to (8)

to the surfaces of teeth, gums and/or **dental** materials fitted in the mouth, then drying it to form a **photocatalytic titanium oxide**-containing **film** on the surf aces, and thereafter exposing the **film** to light.

SUMM [0091] (13) A method for bleaching discolored teeth, which comprises applying the **dental** and oralogic composition of any one of above (1) to (8) to the surfaces of teeth, gums and/or **dental** materials fitted in the mouth, then drying it to form a **photocatalytic titanium oxide**-containing **film** on the surfaces, and thereafter exposing the **film** to light.

SUMM [0092] (14) A method for treating **dental** materials, which comprises applying the **dental** and oralogic composition of any one of above (1) to (8) to the surfaces of **dental** materials not in the mouth, then drying and/or baking it to form a **photocatalytic titanium oxide**-containing **film** on the surf aces of the **dental** materials, and thereafter exposing the **film** to light.

SUMM [0093] (15) Use of the **dental** and oralogic composition of any one of above (1) to (8) for forming a **film**.

SUMM [0094] (16) Use of a **photocatalytic titanium oxide** or a **photocatalytic titanium oxide** precursor for producing a **dental** and oralogic composition.

SUMM [0095] (17) Use of a **photocatalytic titanium oxide** or a **photocatalytic titanium oxide** precursor, and a liquid medium for producing a **dental** and oralogic composition.

SUMM [0096] (18) Use of the following (a) to (a) for producing a **dental** and oralogic composition:

SUMM [0097] (a) a **photocatalytic titanium oxide** or a **photocatalytic titanium oxide** precursor,

SUMM [0098] (b) at least one selected from a **silicon** compound of the following general formula (I): ##STR5##

SUMM [0099] wherein X.sup.1, X.sup.2, X.sup.3 and X.sup.4 each independently represent an alkoxy group or a halogen atom, hydrolyzate of the **silicon** compound (1), a silicone resin, silicone resin precursor and silica, and

SUMM [0101] The "**dental** and oralogic composition" of the invention is meant to include compositions to be applied to teeth; **dental** materials including tooth crown restorative materials, **dentures**, **denture** bases, **denture** rebases, orthodontic bases, wires, bridges, mouth pieces, etc.; gums; **oral** mucous membranes; teeth having been restored with composite resin or coated with **dental** manicure. The **dental** and oralogic composition of the invention is applied to any of those objects to coat them.

SUMM [0102] The **photocatalytic titanium oxide** in the **dental** and oralogic composition of the invention is preferably **titanium oxide** which, when exposed to light, exhibits **photocatalytic** activity to promote the decomposition of organic matters, nitrogen oxides, etc. More preferably the **photocatalytic titanium oxide** is anatase-type titanium dioxide.

SUMM [0103] Depending on the morphology of the **photocatalytic titanium oxide** therein, the **dental** and oralogic composition of the invention is preferably grouped into the following compositions (A) and (B):

SUMM [0104] The **dental** and oralogic composition of this type

contains, as the component (a), a solid **photocatalytic titanium oxide** that exhibits **photocatalytic** activity by itself.

SUMM [0105] Preferably, the **dental** and oralogic composition (A) contains (a) a **photocatalytic titanium oxide**, (b) at least one selected from a **silicon** compound of above formula (1), a hydrolyzate of the **silicon** compound (1), a silicone resin, a silicone resin precursor and silica, and (c) a liquid medium; or contains (a) a **photocatalytic titanium oxide** and (c) a liquid medium.

SUMM [0106] The **dental** and oralogic composition of this type contains, as the component (a), a **photocatalytic titanium oxide** precursor.

SUMM [0107] Preferably, the **dental** and oralogic composition (B) contains (a) a **photocatalytic titanium oxide** precursor, (b) at least one selected from a **silicon** compound of formula (I), a hydrolyzate of the **silicon** compound (1), a silicone resin, a silicone resin precursor and silica, and (c) a liquid medium or contains (a) a **photocatalytic titanium oxide** precursor and (c) a liquid medium.

SUMM [0109] The **photocatalytic titanium oxide** in the composition (A) is preferably in the form of particles (fine powder) having a mean particle size of from. . . 0.005 to 0.1 .mu.m, as it is highly dispersible not forming a sediment while stored or transported, and has high **photocatalytic** activity. These ranges include all values and subranges therebetween, including 0.0015, 0.002, 0.01, 0.05, 0.075, 0.25, 0.35 and 0.45 .mu.m. **Photocatalytic titanium oxide** particles having a smaller particle size ensure higher **photocatalytic** activity. Therefore, in case where the composition (A) containing fine **photocatalytic titanium oxide** particles is directly applied to a predetermined site in the mouth and then exposed to light therein, it does not. . . any strong UV rays. Any weak UV rays that are safe to human bodies will be enough for ensuring the **photocatalytic** activity of the **titanium oxide** in the composition (A). **Titanium oxide** having been prepared in a low-temperature plasma process and therefore having especially high **photocatalytic** activity exhibits its **photocatalytic** activity even when exposed to visible rays of 400 nm or longer. For these reasons, the composition (A) of the. . .

SUMM [0110] The **photocatalytic titanium oxide** content of the composition (A) preferably falls between 0.05 and 40% by weight, more preferably between 0.1 and 20% by weight, in view of the dispersion stability of the ingredient, **photocatalytic titanium oxide** in the composition, the **photocatalytic** activity thereof, the easiness in applying the composition to substrates, and the strength of the coated **film** of the composition. These ranges include all values and subranges therebetween, including 0.07, 0.9, 1.1, 2, 5, 10, 15, 25,. . .

SUMM [0111] Preferably, the **photocatalytic titanium oxide** precursor in the composition (B) includes titanium alkoxides, chelates, acetates, halides, and their hydrolyzates, and one or more of these. . . alkoxides are titanium tetraethoxide, titanium tetrabutoxide, titanium tetra-n-propoxide, titanium tetramethoxide, etc.

One or more of these may be used. Some **titanium oxide** precursors such as titanium tetraethoxide and others are commercially available, for example, as **titanium oxide** sol, and such commercial products are also preferably used.

SUMM [0112] In the **silicon** compound of formula (I) that serves as

the component (b) in the **dental** and oralogic composition of the invention, it is desirable that X.sup.1, X.sup.2, X.sup.3 and X.sup.4 each are independently an alkoxy. . . 1 to 4 carbon atoms, or a halogen atom such as chlorine, bromine or iodine atom. Preferable examples of the **silicon** compound (I) include tetraalkoxysilanes such as tetramethoxysilane, tetraethoxysilane, tetra-n-propoxysilane, tetraisopropoxysilane, tetrabutoxysilane, etc. Hydrolyzates of the **silicon** compound (I) include, for example, silanols derived from the above-mentioned tetraalkoxysilanes and their condensates (alkyl silicates), etc. Combinations of **silicon** compounds (I) may also be used.

SUMM . . . diorganosiloxane units and triorganosiloxane units, those composed of monoorganosiloxane units and triorganosiloxane units, etc. The organic group bonding to the **silicon** atom in the siloxane units includes, for example, alkyl groups such as methyl group, ethyl group, propyl group, butyl group,. . .

SUMM [0116] The **dental** and oralogic composition of the invention may contain, for the component (b), one or more of the above-mentioned **silicon** compounds (I), their hydrolyzates, silicone resins, their precursors, and silica. Though not limited thereto, some preferable examples of the formulation of the **dental** and oralogic composition of the invention are mentioned below.

DETD [0117] (A-1) Composition containing **photocatalytic titanium oxide** particles, and a tetraalkoxysilane or its hydrolyzate in a liquid medium.

DETD [0118] (A-2) Composition containing **photocatalytic titanium oxide** particles, and a silicone resin in a liquid medium

DETD [0119] (A-3) Composition containing **photocatalytic titanium oxide** particles, and a silicone resin precursor such as an organosilane or its hydrolyzate, organosilazane or the like, in a liquid. . .

DETD [0120] (A-4) Composition (suspension) containing **photocatalytic titanium oxide** particles and silica in a liquid medium.

DETD [0121] (A-5) Composition containing a **photocatalytic titanium oxide** in a liquid medium.

DETD [0122] (B-1): Composition containing a **photocatalytic titanium oxide** precursor such as a titanium tetraalkoxide or the like, and a tetraalkoxysilane or its hydrolyzate in a liquid medium.

DETD [0123] (B-2) Composition containing a **photocatalytic titanium oxide** precursor such as a titanium tetraalkoxide or the like, and a silicone resin in a liquid medium.

DETD [0124] (B-3): Composition containing a **photocatalytic titanium oxide** precursor such as a titanium tetraalkoxide or the like, and a silicone resin precursor such as an organosilane or its. . .

DETD [0125] (B-4): Composition containing a **photocatalytic titanium oxide** precursor such as a titanium tetraalkoxide or the like, and silica in a liquid medium.

DETD [0126] (B-5): Composition containing a **photocatalytic titanium oxide** precursor such as a titanium tetraalkoxide or the like, in a liquid medium.

DETD [0127] Preferably, the component (b) in the **dental** and oralogic composition of the invention contains at least 20 mol %, more preferably at least 50 mol % of. . . or its hydrolyzate (a trifunctional or higher functional silane or its hydrolyzate), as it

ensures the mechanical strength of the **film** of the composition. These ranges include all values and subranges therebetween, including 25, 30, 35, 40, 45, 55, 60, 65,. . . of the component (b). Preferably, by use of the crosslinking silane, the composition can form a highly durable and practicable **film** in or not in the mouth, and, in addition, the adhesiveness of the composition to the substrate to which the. . .

DETD [0128] Accordingly, it is preferable that the component (b) in the **dental** and oralogic composition of the invention contains a tetraalkoxysilane and/or its hydrolyzate (for example, as in the composition (A-1) and the composition (B-1) mentioned above), since the composition of the type has good **film**-forming capability and is easy to handle, and since the **film** of the composition formed on teeth, gums, **dental** materials and **oral** mucous membranes has high photocatalytic activity, high mechanical strength and high adhesiveness to substrates.

DETD [0129] In addition, since the **film** of the composition in which the component (b) contains a tetraalkoxysilane and/or its hydrolyzate (especially the composition (A-1) mentioned above). . .

DETD . . . its hydrolyzate. This is because the side product to be formed in hydrolysis and polycondensation of tetraethoxysilane is non-toxic ethyl **alcohol**. Therefore, the composition containing such tetraethoxysilane and/or its hydrolyzate has, in addition to the above-mentioned advantages, an additional advantage of. . .

DETD [0131] In the **dental** and oralogic composition of the invention, the ratio of the **photocatalytic titanium oxide** or **photocatalytic titanium oxide** precursor to at least one selected from a **silicon** compound (I), a hydrolyzate of the **silicon** compound (I), a silicone resin, a silicone resin precursor and silica preferably falls between 20/1 and 1/100 in terms of the molar ratio of titanium atom/ **silicon** atom, as the effect of the composition to decompose **dental plaque** and to retard the formation of **dental plaque** is high. More preferably, the ratio falls between 10/1 and 1/20. These ranges include all values and subranges therebetween, including. . .

DETD [0132] The liquid medium for the **dental** and oralogic composition of the invention may be any and every one safe to human bodies. In general, however, preferred is water, or a mixture of water and **alcohol**, especially ethyl **alcohol**. More preferred for the liquid medium is a mixture of water and **alcohol** in a ratio by volume falling between 1/0.1 and 1/100, since the coatability of the composition containing it is good.. . . 1/1, 1/1.5, 1/2, 1/10, 1/25, 1/30, 1/40, 1/50, 1/70, 1/85 and 1/90. In addition, after the composition containing such a water/**alcohol** mixture as the liquid medium has been applied to teeth, gums, **oral** mucous membranes and **dental** materials to form a **film** thereon, it is easy to remove the liquid medium from the coated composition. However, in case where the composition is not applied directly to the sites in the mouth but is applied to a **dental** material not in the mouth, then the liquid medium is preferably completely removed from the composition to form a **film** on the **dental** material, and thereafter the thus-coated **dental** material is fitted into the intended site in the mouth, any other organic solvent, and preferably not water or **alcohol**, may be used for the liquid medium for the composition. The organic solvent for the liquid medium preferably includes, for example, **acetone**, **methyl ethyl ketone**, **ethyl acetate**, **chloroform**,

toluene hexane, etc.

DETD [0133] The **dental** and oralogic composition of the invention may be in any form of dilute solutions, dilute dispersions, highly viscous solutions, highly viscous dispersions, pastes, shape-forming gels, etc., for which the type and the content of the **photocatalytic titanium oxide** or its precursor and at least one selected from **silicon** compounds (I), their hydrolyzates, silicone resins, silicone resin precursors and silica that constitute the composition shall be appropriately selected and. . .

DETD . . . that a small amount of the composition can be applied to a predetermined site to form a thin and uniform **film** thereon and that, after the **film** is exposed to light to decompose the **dental plaque** around it, washing the cured **film** with water is easy.

DETD [0135] To prepare a highly viscous solution or dispersion of the **dental** and oralogic composition of the invention, or to prepare a paste or a gel of the composition, a thickener may be added to the composition. The thickener easily increases the viscosity of the preparations. One or more of polyvinyl **alcohol**, polyalkylene glycols, glycerin. colloidal silica (silica aerosol, etc.) and the like serving as a thickener can be preferably used. The. . .

DETD [0136] Optionally, the **dental** and oralogic composition of the invention may further contain at least one bactericidal metal component selected from silver, copper and. . . of the substrate to which it has been applied. Accordingly, the composition inhibits more effectively the deposition or adhesion of **dental plaque** onto the site to which it has been applied. In addition, it will be easy to remove **dental plaque** decomposates from the composition applied site through washing with water. The amount of the metal component, if any, in the. . . composition, as enhancing the handleability and the antibacterial and bactericidal effect of the composition and enhancing the durability of the **film** of the composition. This range includes all values and subranges therebetween, including 0.2, 0.5, 0.9, 1.0, 2, 3, 4, 5,. . .

DETD [0137] Also if desired, the **dental** and oralogic composition of the invention may contain a hydrolysis catalyst for the **silicon** compound (1) and the silicone resin precursor, a polycondensation catalyst, a pH controlling agent, a stabilizer, a colorant, a fluoride. . .

DETD [0138] The methods mentioned below are preferably employed for applying the **dental** and oralogic composition of the invention to teeth, gums, **oral** mucous membranes and **dental** materials.

DETD [0139] For example, the composition (A) that contains **photocatalytic titanium oxide** particles may be applied to them according to the following methods:

DETD [0140] (1) The composition (A) is applied to any of teeth, gums, **oral** mucous membranes, **dental** materials (tooth crown restorative materials, **dentures**, **denture** bases, **denture** rebases, orthodontic bases, wires, bridges, mouth places, etc.) fitted in the mouth, or teeth having been restored with composite resin or coated with **dental** manicure, and then optionally dried by exposing it to a gaseous blow (preferably a flowing gas stream) at a temperature not causing damage to the mouth to thereby form a **photocatalytic titanium oxide** -containing **film** on the substrate, and thereafter the **film** is exposed to light to express the **photocatalytic** activity of the **photocatalytic titanium oxide** therein.

DETD [0141] (2) The composition (A) is applied to any of **dental** materials (tooth crown restorative materials, **dentures**, **denture** bases, **denture** rebases, orthodontic bases, wires, bridges, mouth pieces, etc.) not in the mouth, and then optionally dried and/or heated to thereby form a **photocatalytic titanium oxide**-containing **film** on the surface of the **dental** material, thereafter the **film** is exposed to light to express the **photocatalytic** activity of the **photocatalytic titanium oxide** therein, and the **film**-coated **dental** material is fitted into the mouth.

DETD . . . to light are all effected not in the mouth. In this, therefore, the composition (A) having been applied to the **dental** material may be dried and subjected to polycondensation at high temperatures, for example, at above 100.degree. C. Such high-temperature treatment is preferable for ensuring the formation of a tight and abrasion-resistant **film** that contains the **photocatalytic titanium oxide** and silica, on the surface of the **dental** material.

DETD [0143] In the methods (1) and (2). the **film** formed may be exposed to light by the use of a light emitter, but may be exposed to sun light. . .

DETD [0144] In order to convert a **photocatalytic titanium oxide** precursor such as a titanium alkoxide or the like into the corresponding **photocatalytic titanium oxide** (anatase-type titanium dioxide) having **photocatalytic** activity, it is necessary to bake the precursor at a temperature generally falling between 400 and 500.degree. C. These ranges. . . 420, 430, 440, 450, 460, 470, 480 and 490.degree. C. Therefore, in case where the composition (B) is applied to **dental** materials to form thereon a **film** having **photocatalytic** activity, the **dental** materials must bear heating at the baking temperature. For such heat-resistant **dental** materials, for example, used are castable ceramics, **dental** porcelains and metals. A preferred method employable for the composition (B) includes applying the composition (B) to a heat-resistant **dental** material of, for example, castable ceramics, **dental** porcelains or metals (e. g., crowns, inlays, bridges, **dentures**, metal bases, wires, clasps, brackets, etc.), then optionally drying it, thereafter baking it at 400 to 500.degree. C. to thereby convert the **photocatalytic titanium oxide** precursor to the corresponding **photocatalytic titanium oxide** and to form a **film** that contains the thus-converted **photocatalytic titanium oxide** , on the **dental** material, and then exposing the **film** to light to express the **photocatalytic** activity of the **photocatalytic titanium oxide**, and finally fitting the thus-coated **dental** material to a predetermined site in the mouth.

DETD [0145] In place of using the composition (B) that contains a **photocatalytic titanium oxide** precursor along with the component (b) (selected from **silicon** compounds (I), their hydrolyzates, silicone resins, silicone resin precursors and/or silica), a solution or dispersion (including **titanium oxide** sol, etc.) that contains a **photocatalytic titanium oxide** precursor but does not contain the component (b) is also usable in the invention to attain the same result specifically, in case where such a solution or dispersion is applied to

a heat-resistant **dental** material not in the mouth, then baked at 400 to 500.degree. C. and thereafter exposed to light in the same manner as above, a **film** is formed on the **dental** material. Also in this case, the **film** formed on the **dental** material has **photocatalytic** activity, and the cured **film** thereon is effective for decomposing and removing **dental plaque**, for inhibiting **dental plaque** from adhering to the **dental** material, for preventing the **dental** material from being discolored and for preventing and removing **halitosis**. To that effect, the invention also encompasses the method of this case.

DETD [0146] The **photocatalytic** activity of the **photocatalytic titanium oxide**-containing **film** that has been formed on the substrate of, for example, teeth, gums, **oral** mucous membranes, **dental** materials such as tooth crown restorative materials, **dentures**, **denture** bases, **denture** rebases, orthodontic bases, wires, bridges, mouth pieces, etc., and also teeth having been restored with composite resin or coated with **dental** manicure, is ensured to some degree even when the **film** is exposed to ordinary environmental light; however, in order to ensure higher **photocatalytic** activity of the **film** within a shorter period of time, it is preferable that the **film** is forcibly exposed to light by the use of a light emitter. In case where the **photocatalytic** activity of the **film** is lowered with the lapse of time, the **film** may be re-activated by exposing it to light. In particular, if the **film** is repeatedly exposed to light at regular intervals, it surely maintains its **photocatalytic** activity and is therefore extremely effective for inhibiting the deposition of **dental plaque** onto the surface of the **film**-coated substrate, for preventing the discoloration of the substrate, and for preventing **halitosis**. The method is especially preferable for detachable inlays, **dentures**, **denture** bases, cornus bridges, upper structures of implants, mouth pieces, etc,. These coated with the **film** are detached and taken out of the mouth, and may be exposed to light outside of in the mouth.

DETD [0147] The source of light to which the **photocatalytic titanium oxide**-containing **film** is exposed preferably includes an ordinary visible light emitter for **dental** use, **dental** light, and other engineering light emitters, and also mercury lamps, xenon lamps, metal halide lamps, halogen lamps, fluorescent lamps, sun. . .

DETD [0148] Preferably, a **film** that contains a **photocatalytic titanium oxide** is formed on the substrate of, for example, teeth, gums, **oral** mucous membranes, **dental** materials such as tooth crown restorative materials, **dentures**, **denture** bases, **denture** rebases, orthodontic bases, wires, bridges, mouthpieces, etc., as well as teeth having been restored with composite resin or coated with **dental** manicure, and the **film** is then exposed to light to thereby express the **photocatalytic** activity of the **titanium oxide** therein, whereby the **dental plaque** formed on the substrate is decomposed, or deposition of **dental plaque** onto the substrate is retarded. To that effect, the **photocatalytic titanium oxide** -containing **film** formed on the substrate is effective for curing and preventing **dental** and **oral** diseases such as gingivitis, periodontitis and other peridental diseases (pyorrhea alveolaris, etc.), for preventing and retarding discoloration of teeth

and **dental** materials, and for preventing and removing **halitosis**. In addition, the **dental** and oralogic composition of the invention may be applied to discolored teeth in the same manner as described herein, to. . .

DETD [0149] In case where the composition of the invention is again applied to the **oral** mucous membranes, teeth, gums, **dental** materials, and composite resin-restored or **dental** manicure-coated teeth that have been once cleaned with the composition to remove the **dental plaque** therefrom, thereby forming the **photocatalytic titanium oxide** -containing **film** of the composition on them, it is possible to prevent redeposition of **dental plaque** onto these substrates. The durability of the **photocatalytic titanium oxide**-containing **film** in the mouth varies, depending on the site coated with the **film**, but, in general, the **film** can maintain its **photocatalytic** activity at least for a few days to a few weeks or so. Even when the **photocatalytic** activity of the **film** is lowered with the lapse of time, the **film** can be reactivated by again exposing it to light in the manner described hereinabove.

DETD [0151] (1) Preparation of **dental** and oralogic composition:

DETD . . . between 1.5 and 2, and the tetraethoxysilane therein was hydrolyzed to prepare a uniform solution 8 parts by weight of **photocatalytic titanium oxide** particles (Ishihara Sangyo's ST-01, having a mean particle size of 0.007 .mu.n) were added thereto and uniformly dispersed to prepare a **dental** and oralogic composition. This was a dilute dispersion, in which the molar ratio of titanium atom/**silicon** atom was 10/1.

DETD [0153] (2) Production of **denture** base restored with soft rebase:

DETD [0155] (ii) A polymethyl methacrylate **denture** base was polished on its surf ace that shall face an **oral** mucous membrane in its use. The polished depth corresponds to the thickness of the rebase to be applied to this. The polished surface of the **denture** base was coated high with the soft rebase composition that had been prepared in the previous step (i). The **denture** base thus coated high with the soft rebase composition was then fitted in the mouth of the patient, impressed therein, and then taken out of the mouth. The excessive soft rebase composition protruding out of the thus-processed **denture** base was removed. With that, the **denture** base was dipped in water at 25 .degree. C., and exposed to light from a **dental** light emitter (Morita's .alpha.-Light) for 10 minutes, while being shut out of air, to thereby polymerize and cure the soft. . .

DETD [0156] (3) Application of the **dental** and oralogic composition to the **denture** base to form **film** thereon:

DETD [0157] The **denture** base on which the rebase had been polymerized and cured in the above (2)(ii) was taken out of water, and then left at room temperature for 1 day. Next, the **dental** and oralogic composition that had been prepared in the above (1) was applied to the surface of the soft rebase of the **denture** base, and the liquid medium (water and ethanol) was evaporated away. Then, this was dried under heat at 90 to 100.degree. C. for 1 hour, and a **photocatalytic titanium oxide**-containing **film** was thus formed thereon. Next, the **film** was exposed to light from a **dental** light emitter (Morita's .alpha.-Light) for 20 minutes to express the **photocatalytic** activity of the **titanium oxide** therein.

DETD [0158] (4) Fitting of the **denture** base in the mouth and

exposure thereof to light:

DETD [0159] The **denture** base having been coated with the **photocatalytic titanium oxide**-containing **film** in the above (3) was fitted in the mouth of the patient, left as it was therein for 1 week and then taken out. The condition of the rebase of the **denture** bass was macroscopically checked for **plaque** deposition thereon and for discoloration of the rebase. It was found that only slight **plaque** deposited on the surface of the rebase and that the rebase was not discolored. The **plaque** deposited on the surface of the rebase was readily removed by washing with water.

DETD [0160] A **denture** base was coated with the same soft rebase as in the step (2) (ii) in Example 1. In this, however, the soft rebase was not coated with a **photocatalytic titanium oxide**-containing **film**. With that, the **denture** base was fitted in the mouth of the patient, left as it was therein for 1 week and then taken out. The condition of the rebase of the **denture** base was macroscopically checked for **plaque** deposition thereon and for discoloration of the rebase.

DETD [0161] It was found that the amount of the **plaque** deposited on the surf ace of the rebase was much larger than that on the surface of the rebase in. . .

DETD [0162] (1) Preparation of **dental** and oralogic composition:

DETD . . . between 1 and 2, and the tetraethoxysilane therein was hydrolyzed to prepare a uniform solution. 0.8 parts by weight of **photocatalytic titanium oxide** particles (Ishihara Sangyo's ST-01, having a mean particle size of 0.007 .mu.m) were added thereto and uniformly dispersed to prepare a **dental** and oralogic composition. This was a dilute dispersion, which had a **photocatalytic titanium oxide** content of 0.9% by weight and a tetraethoxysilane hydrolyzate content of 2.1% by weight and in which the molar ratio of titanium atom/**silicon** atom was 1/1.

DETD [0164] (2) Formation of **photocatalytic titanium oxide**-containing **film**:

DETD [0166] (ii) The **dental** and oralogic composition having been prepared in the previous stop (1) was applied thin to the surface of the jacket. . . and the solvent was evaporated away. Then, this was heated at 150.degree. C. for 1 hour to thereby form a **photocatalytic titanium oxide**-containing **film** over the jacket crown (Example 2).

DETD . . . the patient was prepared in the same manner as in the step (i), but this was not coated with the **film**, and was directly used as it was (Comparative Example 2).

DETD [0168] (3) Fitting of the jacket crown in the mouth and check for **plaque** deposition thereon:

DETD [0169] (i) The jacket crown (this was prepared in the previous step (2) (ii) and was coated with the **photocatalytic titanium oxide**-containing **film**) was fitted to the right-side, admaxillary central incisor of the anterior teeth of the patient, by the use of a **dental** resin cement (Kuraray's Panavia) In addition, the jacket crown (this was prepared in the previous step (2) (iii) and was not coated the **photocatalytic titanium oxide**-containing **film**) was fitted to the left-side, admaxillary central incisor of the anterior teeth of the patient, also by the use of the same **dental** resin cement as above.

DETD [0170] (ii) After three months, the patient was recalled, and a **plaque**-staining liquid (Lion's **Plaque** Tester) was applied to its anterior teeth. With that, the surfaces of the jacket crowns were macroscopically checked for **plaque** deposition thereon. Little **plaque** deposition was seen on the jacket crown (this had the **photocatalytic titanium oxide** -containing **film** formed thereon) fitted to the right-side, admaxillary central incisor of the anterior teeth of the patient; but much **plaque** deposition was seen on and around the jacket crown (this did not have the **photocatalytic titanium oxide**-containing **film**) fitted to the right-side, admaxillary central incisor of the anterior teeth of the patient, from the cervical margin to the. . .

DETD . . . parts by weight of titania sol (Ishihara Sangyo's STS-01) this is an aqueous sol that contains 30% by weight of **titanium oxide** having a mean particle size of 0. 007 .mu.m), 70 parts by weight of ethanol and 2 parts by weight of water were mixed to prepare a **dental** and oralogic composition. This was a dilute liquid, which had a **photocatalytic titanium oxide** content of 0.8% by weight and a tetraethoxysilane content of 1.3% by weight and in which the molar ratio of titanium atom/**silicon** atom was 5/3.

DETD [0172] (2) The **dental** and oralogic composition having been prepared in the previous step (1) was applied to the admaxillary central incisor of the. . . the use of a brush, and a light air blow was applied thereto to remove the liquid medium (water and **alcohol**) . Using a **dental** light emitter (Ushio Electric's Litel), the area coated with the **dental** and oralogic composition was uniformly exposed to light for 2 minutes, and then washed with water. The process of applying the **dental** and oralogic composition, drying it with an air blow, exposing it to light and washing it with water was repeated. . .

DETD [0173] (3) Three days after the treatment of the above (2), the treated part was stained with a **plaque**-staining liquid (Lion's **Plaque** Tester), and macroscopically checked for **plaque** deposition thereon. **Plaque** deposition on the site coated with the **dental** and oralogic composition was significantly smaller than that on the site not coated with it. The result confirms that the **dental** and oralogic composition prepared in the above (1) is effective for removing **plaque** and for inhibiting re-deposition of **plaque**.

DETD [0174] (1) To the **dental** and oralogic composition having been prepared in the same manner as in the step (1) in Example 3, added was 0.1% by weight, relative to the weight of the composition, of polyvinyl **alcohol**, and dissolved therein to prepare a paste of the composition.

DETD [0175] (2) The **dental** and oralogic paste that had been prepared in the previous step (1) was applied to the cervical margin and the gingival margin around the admaxillary and mandibular central incisors of a patient, and exposed to light from a **dental** light emitter (Ushio Electric's Litel) for 3 minutes.

DETD [0176] (3) Three days after the treatment of the above (2), the treated part was stained with a **plaque**-staining liquid (Lion's **Plaque** Tester) , and macroscopically checked for **plaque** deposition thereon. **Plaque** deposition on the site coated with the **dental** and oralogic paste was significantly smaller than that on the site not coated with it. The result confirms that the

dental and oralogic paste prepared in the above (1) is effective for removing **plaque** and for inhibiting re-deposition of **plaque**.

DETD [0177] (1) To the **dental** and oralogic paste having been prepared in the step (1) in Example 4, further added was 2% by weight, relative. . . weight of the paste, of fine silver particles (having a mean particle size of 2 .mu.m) to prepare a silver-containing **dental** and oralogic paste.

DETD [0178] (2) The silver-containing **dental** and oralogic paste that had been prepared in the previous step (1) was applied to the cervical margin and the. . . mandibular central incisors of a patient and to the pockets below the gingival margin, and exposed to light from a **dental** light emitter (Ushio Electric's Litel) for 3 minutes.

DETD [0179] (3) Three weeks after the treatment of the above (2), the treated part was stained with a **plaque**-staining liquid (Lion's **Plaque** Tester) , and macroscopically checked for **plaque** deposition thereon. **Plaque** deposition on the site coated with the **dental** and oralogic paste was significantly smaller than that on the site not coated with it. In addition, a small amount of the tissue of the part coated with the **dental** and oralogic paste was collected and checked for deposition of bacteria of Streptococcus mutans and Candida alubicans. Little deposition of the bacteria on the site was seen. The results confirm that the **dental** and oralogic composition that contains a **photocatalytic titanium oxide** and a **silicon** compound (i) along with fine silver particles is more effective for preventing and retarding **dental plaque** deposition and for killing bacteria.

DETD [0180] (1) From a metal frame of gold-silver-palladium alloy (GC's Castwell MC) and a **dental** porcelain (Shoflisha's Unibond Vintage), prepared was a metal-bonded porcelain bridge for admaxillary teeth.

DETD [0181] (2) The metal-bonded porcelain bridge that had been prepared in the previous step (1) was sprayed thin with **titanium oxide** sol (Ishihara Sangyo's STS-01, having a **titanium oxide** content of 30% by weight), then dried, and baked at 500.degree. C. Thus, this was coated with **photocatalytic titanium oxide** (anatase-type titanium dioxide).

DETD . . . step (2) was fitted into the mouth of a patient. After a half year, this was macroscopic ally checked for **plaque** deposition thereon, but little **plaque** deposited on it,

DETD . . . a mean molecular weight of about 4000, both serving as a thickener, and uniformly dispersed therein to prepare an adhesive, **dental** and oralogic paste.

DETD [0184] (2) The **dental** and oralogic paste having been prepared in the above stop (1) was applied to all the teeth of a patient,. . . to the central incisor and also the gingival margin and the gums therearound, and was exposed to light from a **dental** light emitter (Ushio Electric's Litel) for 10 minutes.

DETD . . . with it (this corresponds to the area from the left-side admaxillary premolar to the central incisor) were macroscopically checked for **plaque** deposition thereon, by the use of a **plaque**-staining liquid (Lion's **Plaque** Tester). The **plaque** deposition on the site coated with the paste was significantly smaller than that on the site not coated with it.

DETD [0186] The bacteria inspection test made on the **plaque** that had been collected from the site coated with the paste revealed that

bacteria of P. gingivalis and St. mutans were killed in the **plaque**.

DETD . . . (1) 20 parts by weight of water, 40 parts by weight of glycerin, 10 parts by weight of the same **photocatalytic titanium oxide** powder as in Example 1, and 10 parts by weight of a silica fine powder (Aerosil 130) were mixed and uniformly dispersed to obtain a viscous **dental** and oralogic composition.

DETD [0188] (2) The **dental** and oralogic composition having been prepared in the previous step (1) was applied thin to a right-half of an extracted. . . comparison as it was, without applying the composition. Then, the tooth was exposed to light for 5 minutes using a **dental** light emitter (Uni XSII, manufactured by Kulzer) and washed with water to remove the applied composition.

DETD [0189] (3) After repeating the same operation as in the previous step (2) three times, the site applied with the **dental** and oralogic composition of this invention was compared in color tone through visual observation with the side not applied with it. As a result, in the site applied with the **dental** and oralogic composition of this invention, the original pale brown color became a pale yellow to white color, while in. . . applied with it, the color tone was not changed, i.e., the original brown color retained. The result confirms that the **dental** and oralogic composition of this invention is also effective for the purpose of bleaching the discolored tooth.

DETD . . . the same manner as in the step (1) in Example 7. In this, however, the paste prepared did not contain **photocatalytic titanium oxide** particles.

DETD . . . step (1) was applied to the mouth of a patient, exposed to light, washed with water, and macroscopically tested with **Plaque** Tester for **plaque** deposition in the mouth. There was found no significant difference in the **plaque** deposition between the paste-coated site and the site not coated with the paste.

DETD [0192] As described in detail hereinabove with reference to its preferred embodiments, the **dental** and oralogic composition of the invention is applied to teeth, gums, **dental** materials in the mouth, and teeth restored with composite resin or coated with **dental** manicure to prevent **dental plaque** deposition on them and even to promote destruction and removal of the **dental plaque** deposited an them, thereby effectively preventing and curing **oral** diseases and **dental** diseases such as **dental caries**, gingivitis, periodontitis and other peridontal diseases (pyorrhea alveolaris, etc.), stomatitis, etc.

DETD [0193] In addition, the **dental** and oralogic composition of the invention effectively prevents or retards the discoloration of teeth and **dental** materials to be caused by adhesion of cigarette tar or food deposits thereto.

DETD [0194] Further, the **dental** and oralogic composition of the invention is effectively used for bleaching discolored teeth.

DETD [0195] Further, the **dental** and oralogic composition of the inventions effective for preventing and removing **halitosis**.

DETD [0196] Further, the **dental** and oralogic composition of the invention is easy to handle and is safe.

DETD [0197] Further, according to the method of the invention, a **film** effective for preventing and curing the **dental** diseases mentioned above, for preventing and retarding the discoloration of **dental** materials, for bleaching discolored teeth and for

preventing **halitosis** can be easily formed on **dental** materials in and not in the mouth.

DETD [0198] The **dental** and oralogic composition is capable of inhibiting **dental plaque** deposition and decomposing **dental plaque** to thereby prevent and cure **dental** diseases and **oral** diseases such as **dental caries**, gingivitis, periodontitis and other peridental diseases (pyorrhea alveolaris, etc.), stomatitis, etc., and is effective for preventing discoloration of teeth and **dental** materials and for preventing and removing **halitosis**; and the composition is particularly suitable for **dental** and **oral** care. The **dental** and oralogic composition preferably contains a **photocatalytic titanium oxide** or its precursor; at least one selected from **silicon** compounds such as tetraalkoxysilanes, silicone resins and their precursors and silica, and a liquid medium; or it contains a **photocatalytic titanium oxide** or its precursor and a liquid medium. The method for **oral** and **dental** care includes applying the composition to teeth, gums, **oral** mucous membranes or **dental** materials in the mouth, or applying the composition to **dental** materials not in the mouth, to thereby fix **photocatalytic titanium oxide** on them or form a **photocatalytic titanium oxide**-containing **film** on them.

CLM What is claimed is:

1. A composition, comprising: (a) a **photocatalytic titanium oxide** or a **photocatalytic titanium oxide** precursor; (b) at least one selected from the group consisting of: a **silicon** compound having the following formula (I): ##STR6## wherein X.sup.1, X.sup.2, X.sup.3 and X.sup.4 each independently represent an alkoxy group or a halogen atom, a hydrolyzate of said **silicon** compound (I), a silicone resin, silicone resin precursor and silica; and (c) a liquid medium.

. . . ratio of (a) to (b) ranges from 20/1 to 1/100 in terms of moles of titanium atoms in (a)/moles of **silicon** atoms in (b).

3. The composition as claimed in claim 1, wherein the **photocatalytic titanium oxide** precursor in (a) is a titanium alkoxide.

5. The composition as claimed in claim 1, which is a **dental** and oralogic composition.

. . . 6. The composition as claimed in claim 1, wherein said liquid medium is selected from the group consisting of water, **alcohol**, a mixture of water and **alcohol**, **acetone**, **methyl ethyl ketone**, **ethyl acetate**, **chloroform**, **toluene**, **hexane**, and combinations thereof.

9. A **dental** and oralogic composition, comprising a **photocatalytic titanium oxide** or a **photocatalytic titanium oxide** precursor.

10. A **dental** and oralogic composition, comprising a **photocatalytic titanium oxide** or a **photocatalytic titanium oxide** precursor, and a liquid medium.

11. A **film**, comprising the composition as claimed in claim 1.

12. The **film** as claimed in claim 11, which is present on a surface of at least one selected from the group consisting of teeth, gums, **dental** materials fitted in the mouth, **oral** mucous membranes, **dental** materials not in the mouth, tooth crown restorative materials, **dentures**, **denture** bases, **denture** rebases, orthodontic bases, wires, bridges, mouth pieces, teeth restored with composite resin, teeth coated with **dental** manicure, and combinations thereof.

13. A method for making a **film**, comprising applying the composition as claimed in claim 1 to a surface of at least one selected from the group consisting of teeth, gums, **dental** materials fitted in the mouth, **oral** mucous membranes, **dental** materials not in the mouth, and combinations thereof.

14. A method for preventing or curing **oral** diseases or **dental** diseases, which comprises: applying the composition as claimed in claim 1 to a surface of at least one selected from the group consisting of teeth, gums, **dental** materials fitted in the mouth, **oral** mucous membranes, **dental** materials not in the mouth, and combinations thereof, to form an applied composition; drying said applied composition to form a **photocatalytic titanium oxide**-containing **film** on said surface; and exposing said **film** to light.

15. A method for preventing or removing **halitosis**, which comprises: applying the composition as claimed in claim 1 to a surface of at least one selected from the group consisting of teeth, gums, **dental** materials fitted in the mouth, **oral** mucous membranes, **dental** materials not in the mouth, and combinations thereof, to form an applied composition; drying said applied composition to form a **photocatalytic titanium oxide**-containing **film** on said surface; and exposing said **film** to light.

16. A method for preventing or retarding the discoloration of teeth or **dental** materials, which comprises: applying the composition as claimed in claim 1 to a surface of at least one selected from the group consisting of teeth, gums, **dental** materials fitted in the mouth, **oral** mucous membranes, **dental** materials not in the mouth, and combinations thereof, to form an applied composition; drying said applied composition to form a **photocatalytic titanium oxide**-containing **film** on said surface; and exposing said **film** to light.

. . . as claimed in claim 1 to a surface of at least one selected from the group consisting of teeth, gums, **dental** materials fitted in the mouth, **oral** mucous membranes, **dental** materials not in the mouth, and combinations thereof, to form an applied composition; drying said applied composition to form a **photocatalytic titanium oxide**-containing **film** on said surface; and exposing said **film** to light.

18. A method for treating **dental** materials, which comprises: applying the composition as claimed in claim 1 to a surface of a **dental** material, to form an applied composition; drying or baking or drying and baking said applied composition to form a **photocatalytic titanium oxide**-containing

film on said surface; and exposing said **film** to light.

19. The method as claimed in claim 18, wherein said **dental** material is not in a mouth.

20. A method for producing a **dental** and oralogic composition, comprising admixing a **photocatalytic titanium oxide** or a **photocatalytic titanium oxide** precursor with said **dental** and oralogic composition.

21. A **film**, produced by a process comprising: applying the composition as claimed in claim 1 to a surface, to form an applied composition; and drying or baking or drying and baking said applied composition to form a **photocatalytic titanium oxide**-containing **film** on said surface.

22. The **film** as claimed in claim 21, wherein said surface is a surface of at least one selected from the group consisting of teeth, gums, **dental** materials fitted in the mouth, **oral** mucous membranes, **dental** materials not in the mouth, tooth crown restorative materials, **dentures**, **denture** bases, **denture** rebases, orthodontic bases, wires, bridges, mouth pieces, teeth restored with composite resin, teeth coated with **dental** manicure, and combinations thereof.

23. An article, comprising a surface and the **film** as claimed in claim 21 in contact with said surface.

24. A method for preparing a **dental** and oralogic composition, comprising admixing: (a) a **photocatalytic titanium oxide** or a **photocatalytic titanium oxide** precursor; (b) at least one selected from the group consisting of: a **silicon** compound having the following formula (I): ##STR7## wherein X.sup.1, X.sup.2, X.sup.3 and X.sup.4 each independently represent an alkoxy group or a halogen atom, a hydrolyzate of said **silicon** compound (I), a silicone resin, silicone resin precursor and silica; and (c) a liquid medium.

L22 ANSWER 3 OF 5 USPATFULL
AN 2000:173885 USPATFULL
TI Photocatalytically hydrophilifiable coating composition
IN Hayakawa, Makoto, Kitakyushu, Japan
Kanno, Mitsuyoshi, Kitakyushu, Japan
PA Toto Ltd., Fukuoka-ken, Japan (non-U.S. corporation)
PI US 6165256 20001226
AI US 1999-232494 19990115 (9)
RLI Continuation of Ser. No. WO 1997-JP2467, filed on 16 Jul 1997
PRAI JP 1996-221641 19960719
JP 1996-266554 19960831
JP 1996-285796 19960920
JP 1996-355953 19961224
JP 1997-13048 19970108
JP 1997-55533 19970224
JP 1997-93232 19970326
DT Utility
FS Granted
EXNAM Primary Examiner: Brunsman, David
LREP Jones, Day, Reavis & Pogue

CLMN Number of Claims: 22
ECL Exemplary Claim: 1
DRWN 7 Drawing Figure(s); 6 Drawing Page(s)
LN.CNT 1495
CAS INDEXING IS AVAILABLE FOR THIS PATENT.
AB A composition is disclosed which can hydrophilify the surface of a member to impart an antifogging property to the surface of the member. The composition for hydrophilifying the surface of the member comprises at least (a) photocatalytic particles of a metallic oxide, (b) a precursor capable of forming a silicone resin **film** or a precursor capable of forming a silica **film**, and (c) a solvent, the total content of the photocatalytic particle and the solid matter of the precursor in the composition being 0.01 to 5% by weight. The hydrophilic property can be imparted simply by applying the composition onto a member and drying or heating the composition applied to the member. The resultant hydrophilic thin **film** is transparent and, hence, does not sacrifice the transparency and appearance of a member required to be transparent. Further, the surface of a member with the above composition applied thereto has such a property that water droplets adhered thereon can be immediately removed by vaporization and the surface is less likely to be soiled and, even when a contaminant is adhered thereon, can easily release the contaminant therefrom.

AB . . . member comprises at least (a) photocatalytic particles of a metallic oxide, (b) a precursor capable of forming a silicone resin **film** or a precursor capable of forming a silica **film**, and (c) a solvent, the total content of the photocatalytic particle and the solid matter of the precursor in the. . . applying the composition onto a member and drying or heating the composition applied to the member. The resultant hydrophilic thin **film** is transparent and, hence, does not sacrifice the transparency and appearance of a member required to be transparent. Further, the. . .

SUMM . . . difficult to ensure the field of vision and, hence, is detrimental to traffic safety for vehicles. Fogging of endoscopic lenses, **dental** mirrors, and converging lenses for laser **dental** treatment equipment will place an obstacle on proper diagnosis, operation, and treatment. Fogging of cover glasses for instrument boards renders. . .

SUMM . . . at least one selected from a group consisting of silica fine particles, a precursor capable of forming a silicone resin **film** and a precursor capable of forming a silica **film**, and

DETD . . . member and drying or heating the composition applied to the surface. It is, of course, expected that a variation in **film** thickness or uneven application is created depending upon methods for applying the composition onto the surface of members. According to. . . the composition of the present invention, however, regulation of the amount of the composition applied so as to give a **film** thickness described below and selection of the method for applying the composition so as to give an even **film** permits the above excellent hydrophilic surface to be formed very simply.

DETD . . . of the surface provided by the composition of the present invention does not depend upon the thickness of the thin **film** provided by the composition of the present invention. It is already known that a photocatalyst has oxidative degradation activity and a thin **film** containing a photocatalyst has antisoiling, antibacterial, and deodorant effects based on such activity. The present inventors have

confirmed that this oxidative degradation activity depends upon the thickness of the **film** containing the photocatalyst. Further, the present inventors have confirmed that the hydrophilification derived from the composition of the present invention can be developed even in a such a **film** thickness that the oxidative degradation activity is very low or is absent. Furthermore, the present inventors have confirmed that, in such a small thickness, of the **film** provided by the composition of the present invention, as will not influence the transparency of a transparent member, the oxidative. . .

DETD . . . less than 0.001 mW/cm.sup.2, more preferably not less than 0.01 mW/cm.sup.2, most preferably not less than 0.1 mW/cm.sup.2 When the **photocatalytic** oxide is anatase form of **titanium oxide**, rutile form of **titanium oxide**, zinc oxide, or strontium titanate, sunlight, a room lamp, a fluorescent lamp, a mercury lamp, an incandescent lamp, a xenon. . . the like may be suitably utilized as the light source for photoexcitation of the photocatalyst. On the other hand, the **photocatalytic** oxide is tin oxide, a-bactericidal lamp, a BLB lamp and the like are suitably used.

DETD . . . hydrophilified surface provided by the composition of the present invention, the condensed water is likely to form a uniform water **film** without forming discrete water drops. Therefore, no light scattering fog is likely to be created on the surface of the. . . which obstruct the view, because water droplets adhered on the surface of these articles rapidly spread into an even water **film**. This permits a high level of view and visibility to be ensured, which in turn ensures traffic safety for vehicles. . .

DETD . . . members to which the composition may be applied include mirrors, such as rearview mirrors for vehicles, bathroom mirrors, lavatory mirrors, **dental** mouth mirrors, reflecting mirrors for roads; lenses, such as eyeglass lenses, optical lenses, lighting lenses, lenses for semiconductors, lenses for. . . foods, such as Chinese bun; covers for measuring instruments, covers of rearview camera lenses for vehicles, converging lenses for laser **dental** treatment equipments, covers of sensors for laser beam detection, such as sensors for vehicular gaps, covers of infrared sensors; filters. . .

DETD . . . at least one selected from a group consisting of silica fine particles, a precursor capable of forming a silicone resin **film** and a precursor capable of forming a silica **film**, and

DETD The **photocatalytic** particles contained in the composition according to the present invention basically comprise a metallic oxide. Specifically, in the present invention,. . . the crystal, can cause excitation (photoexcitation) of electrons in the valence band to produce a conduction electron and a hole. **Photocatalytic** oxides usable herein include, for example, anatase form of **titanium oxide**, rutile form of **titanium oxide**, zinc oxide, tin oxide, ferric oxide, dibismuth trioxide, tungsten trioxide, and strontium titanate.

DETD Silica fine particles and Precursor of silicone resin **film** and silica **film**

DETD One preferred example of the precursor capable of forming a silica

film which may be used in the composition of the present invention is a silicate represented by the following average composition. . .

DETD One preferred example of the precursor, of a silicone coating, capable of forming a silicone **film** which may be used in the composition of the present invention is a siloxane represented by the average composition formula:

DETD One preferred example of the precursor capable of forming a silicone **film** which may be used in the composition of the present invention is a hydrolyzable silane derivative represented by the general. . .

DETD . . . usable herein include water, an organic solvent, and a mixed solvent composed of water and an organic solvent. Water, an **alcohol**, or a mixed solvent composed of water and an **alcohol** is particularly preferred.

DETD According to a preferred embodiment of the present invention, use of an **alcohol**, which has a molecular weight of 60 to 300, preferably a molecular weight of 60 to 100 and is liquid. . .

DETD Examples of preferred alcohols usable herein include methanol, ethanol, n-propanol, isopropanol, t-butanol, isobutanol, n-butanol, 2-methylpropanol, pentanol, ethylene glycol, monoacetone **alcohol**, diacetone **alcohol**, ethylene glycol monomethyl ether, 4-hydroxy-4-methyl-2-pentanone, dipropylene glycol, propylene glycol, tripropylene glycol, 1-ethoxy-2-propanol, 1-butoxy-2-propanol, 1-propoxy-2-propanol, propylene glycol monomethyl ether, dipropylene glycol. . .

DETD . . . the application of the composition onto the member. In particular, when the composition according to the present invention contains an **alcohol**, the addition of the surfactant is preferred. In some cases, several hours are necessary for achieving the photo-hydrophilification of the surface with the composition of the present invention applied thereto. In this case, when the **alcohol** derived from the composition of the present invention remains on the surface, the hydrophilification of the surface is often unsatisfactory. . .

DETD . . . when the composition of the present invention is applied to a large article. Examples of preferred levelling agents include diacetone **alcohol**, ethylene glycol monomethyl ether, 4-hydroxy-4-methyl-2-pentanone, dipropylene glycol, tripropylene glycol, 1-ethoxy-2-propanol, 1-butoxy-2-propanol, propylene glycol monomethyl ether, 1-propoxy-2-propanol, dipropylene glycol monomethyl ether,. . .

DETD . . . is to be imparted, and the composition applied to the surface is then dried or cured to form a thin **film**.

DETD As described above, preferably, the composition of the present invention is finally brought to a thin **film** having a thickness of not more than 0.4 .mu.m, preferably not more than 0.2 .mu.m, on a member. In order to form such a thin **film**, the composition of the present invention is applied onto the surface of the member at a coverage of preferably about. . .

DETD The composition after the application onto the surface of the member is then dried or cured to form a thin **film**. The term "dried or cured" used herein means that the precursor of silica or the precursor of silicone contained in. . .

DETD Precursor of silica **film** and amount of solvent

DETD This demonstrates that addition of a surfactant in addition to **photocatalytic titanium oxide** particles, silica, and ethanol offers not only a permanent antifogging property but

also an initial antifogging property.

DETD . . . added thereto in an amount as small as 0.4 part by weight based on one part by weight of the **photocatalytic titanium oxide** particle, the loss time was about 2 hr, and, for the sample prepared by coating the coating liquid sample B3. . . surfactant being added thereto in an amount of 10 parts by weight based on one part by weight of the **photocatalytic titanium oxide** particles, the temporary loss time of the antifogging property was 200 hr or more.

DETD A **titanium oxide** sol (ST-K01) and a **titanium oxide** sol (ST-K03) (solid content 10% by weight; the solute being composed of 5 parts by weight of **titanium oxide** (anatase form) and 5 parts by weight of an alkyl silicate) were mixed together in a ratio of 1:1, and the mixture was diluted 20 times with propanol to prepare a **photocatalytic** coating sample B5. Sorbitan monocaprylate (a nonionic surfactant) was added in an amount of 0.05% by weight (that is, 0.325% by weight based on **titanium oxide**) to this sample B5 to prepare a sample B6. Sorbitan monocaprylate was added in an amount of 0.1% by weight (that is, 0.65% by weight based on **titanium oxide**) to the sample B5 to prepare a sample B7. A quaternary ammonium salt (a cationic surfactant) was added in an. . .

DETD Addition of **alcohol** for a small subject

DETD Addition of **alcohol** for large subject

DETD Addition of **alcohol** for large subject

DETD Addition of **alcohol** for large subject

DETD Addition of **alcohol** for large subject

DETD . . . in a ratio of 1:1, and the mixture was diluted 25 times with a 9:1 mixture of 2-propanol and diacetone **alcohol** (4-hydroxy-4-methyl-pentanone) to prepare a coating liquid sample D11 (pH 4).

DETD . . . in a ratio of 1:1, and the mixture was diluted 25 times with a 9:1 mixture of ethanol and diacetone **alcohol** to prepare a coating liquid sample D13.

DETD . . . a ratio of 1:1, and the mixture was diluted 25 times with a 8:1:1 mixture of ethanol, 2-propanol, and diacetone **alcohol** to prepare a coating liquid sample D15.

CLM What is claimed is:

. . . composition for hydrophilifying the surface of a member, comprising at least (a) photocatalytic particles of a metallic oxide, (b) a **silicon**-based component selected from the group consisting of silica fine particles, a precursor capable of forming a silica **film** and combinations thereof, and (c) a solvent, wherein the total content of the photocatalytic particles and the **silicon** in the **silicon**-based component in the composition is 0.01 to 1% by weight.

5. The composition according to any one of claims 1 to 3, wherein the **photocatalytic** particles are constituted by the anatase form of **titanium oxide**.

7. The composition according to any one of claims 1 to 3, wherein the solvent is an **alcohol**.

14. The composition according to any one of claims 1 to 3, wherein the **photocatalytic** oxide is selected from the group consisting of anatase form of **titanium oxide**, rutile form of **titanium oxide**, zinc oxide, tin oxide, ferric oxide,

dibismuth trioxide, tungsten trioxide, and strontium titanate.

16. The composition according to claim 14, which, when applied to the surface of a member to form a **film**, permits condensed water of moisture and/or water droplets adhered onto the surface to be spread on the **film**, thereby enabling the **film** to prevent the surface from being fogged or clouded by the condensed water of moisture and/or the water droplets.

17. The composition according to claim 14, which, when applied to the surface of a member to form a **film**, enables a contaminant adhered onto the surface to be easily washed away by water.

22. The composition according to any one of claims 1 to 3, wherein the precursor of a silica **film** is selected from the group consisting of tetramethoxysilane, tetraethoxysilane, tetrapropoxysilane, tetrabutoxysilane, diethoxydimethoxysilane, tetrachlorosilane, tetrabromosilane, silanol, and dimethoxydiethoxysilane, and partial hydrolyzates. . .

L22 ANSWER 4 OF 5 USPATFULL
AN 1999:96145 USPATFULL
TI Photocatalytically hydrophilifying and hydrophobifying material
IN Hashimoto, Kazuhito, Yokohama, Japan
Fujishima, Akira, Kawasaki, Japan
Watanabe, Toshiya, Kitakyushu, Japan
Shimohigoshi, Mitsuhide, Kitakyushu, Japan
Hayakawa, Makoto, Kitakyushu, Japan
PA Toto Ltd., Fukuoka-Ken, Japan (non-U.S. corporation)
PI US 5939194 19990817
AI US 1997-987670 19971209 (8)
RLI Continuation-in-part of Ser. No. US 1997-933886, filed on 19 Sep 1997
PRAI JP 1996-344584 19961209
JP 1997-256090 19970904
DT Utility
FS Granted
EXNAM Primary Examiner: Lusignan, Michael
LREP Jones, Day, Reavis & Pogue
CLMN Number of Claims: 18
ECL Exemplary Claim: 4
DRWN 11 Drawing Figure(s); 7 Drawing Page(s)
LN.CNT 861
CAS INDEXING IS AVAILABLE FOR THIS PATENT.
AB A method for highly hydrophilifying the surface of an article by photoexcitation of a semiconductor photocatalyst and maintaining the hydrophilicity is disclosed. A layer containing a photocatalyst is formed on a substrate. Onto the surface of the layer are fixed a hydroxyl group upon photoexcitation of the photocatalyst and a physically adsorbed water molecule in the vicinity of the hydroxyl group upon photoexcitation of the photocatalyst. Thus, the surface is highly hydrophilified. Further, this surface, simultaneously with the hydrophilification, exhibits higher hydrophobicity.
DRWD FIG. 8 is a graph showing a change in contact angle of the surface of a **photocatalytic titanium oxide** layer with water upon irradiation of the surface of the **photocatalytic titanium oxide** layer with ultraviolet light having different wavelengths as a function of light irradiation time, this change having been determined in. . .

DETD . . . to proceed as follows. At the outset, irradiation of the photocatalyst with excitation light causes a metal atom in the **photocatalytic** oxide to be reduced. For example, in the case of **titanium oxide**, tetravalent (+4) titanium is reduced to trivalent (+3) titanium to create a vacancy lacking in oxygen on the surface. This. . .

DETD . . . or tetrabutoxytitanium), titanium acetate, or a titanium chelate, and the mixture is diluted with a nonaqueous solvent, such as an **alcohol** (such as ethanol, propanol, or butanol). While partially progressing hydrolysis or after complete hydrolysis, the mixture is coated by spray. . .

DETD . . . or tetrabutoxytitanium), titanium acetate or a titanium chelate, and the mixture is diluted with a nonaqueous solvent, such as an **alcohol** (such as ethanol, propanol, or butanol). While partially progressing hydrolysis or after complete hydrolysis, the mixture is coated by spray. . .

DETD . . . titanium oxide by irradiation with light including an ultraviolet radiation, at least a part of organic groups bonded to the **silicon** atom in the silicone molecule is substituted by a hydroxyl group, and a physically adsorbed water layer is further formed.

. .

DETD . . . have antifogging effect, examples of substrates usable herein include: mirrors, such as rearview mirrors for vehicles, bathroom mirrors, lavatory mirrors, **dental** mouth mirrors, reflecting mirrors for roads; lenses, such as eyeglass lenses, optical lenses, lenses for cameras, lenses for endoscopes, lighting. . .

DETD A thin **film** of a rutile titanium oxide single crystal was allowed to stand in the dark for 2 months to prepare sample. . .

L22 ANSWER 5 OF 5 USPATFULL

AN 97:86362 USPATFULL

TI Photoreactive noxious substance purging agent and photoreactive noxious substance purging material using the agent

IN Takaoka, Kazuchiyo, Tokyo, Japan
Hyodo, Kenji, Tokyo, Japan
Ebihara, Isao, Tokyo, Japan
Oku, Yasuyuki, Tokyo, Japan
Ohgami, Katsushi, Tokyo, Japan

PA Mitsubishi Paper Mills Limited, Tokyo, Japan (non-U.S. corporation)

PI US 5670247 19970923

AI US 1995-535917 19950928 (8)

PRAI JP 1994-238866 19941003
JP 1994-247990 19941013
JP 1994-300961 19941205
JP 1995-8425 19950123

DT Utility

FS Granted

EXNAM Primary Examiner: Le, H. Thi

LREP Foley & Lardner

CLMN Number of Claims: 19

ECL Exemplary Claim: 17

DRWN 2 Drawing Figure(s); 2 Drawing Page(s)

LN.CNT 1913

AB Disclosed is a photoreactive noxious substance purging agent comprising a photoreactive semiconductor, a carrier, and a microfibrillated microfiber. In this photoreactive noxious substance purging agent, loss of the photoreaction effective surface of the photoreactive semiconductor can be held down to the minimum and a sufficient noxious substance removing characteristics can be exhibited.

SUMM . . . et al report in J. Oil. Chem. Assoc., 61, 351 (1978) that when ultraviolet light is irradiated using titanium oxide, **alcohol** in the mixed system of water and **alcohol** is decomposed. Furthermore, Japanese Patent Kokai No. 61-135669 discloses a process of decomposing sulfur compounds which are malodorous substances by. . .

SUMM Moreover, Japanese Patent Kokoku No. 2-62297 discloses a process of removing low concentration nitrogen oxides using a mixture of **titanium oxide** and active carbon. The decomposition of malodorous substances with photoreactive semiconductors such as **titanium oxide** and zinc oxide is based on **photocatalytic** oxidizing action of the photoreactive semiconductors on the malodorous substances contacting with the semiconductors due to excitation with activation rays.. . .

SUMM . . . photoreactive semiconductor on a specific latex. There is also the problem that the photoreactive semiconductor is buried in the latex **film**, and the effective surface area of the photoreactive semiconductor decreases. Furthermore, Japanese Patent Kokai No. 4-256755 discloses a method of. . .

DETD . . . same will be explained in detail below. The photoreactive semiconductors used in the present invention are semiconductors which induce a **photocatalytic** reaction and have a width of forbidden band of 0.5-5 eV, preferably 1-4 eV. As examples of these photoreactive semiconductors. . . used in the present invention, mention may be made of particles of metal oxides such as zinc oxide, tungsten oxide, **titanium oxide**, cerium oxide, etc. Among them, **titanium oxide** is most suitable for use in life space from the points of structural stability, photoreactive noxious substance removing ability and. . .

DETD . . . are used preferably in the present invention are very small in particle size as mentioned above, and are poor in **film** -formability when used singly, the photoreactive semiconductors held in the matrix of photoreactive noxious substance purging material fall off shortly and. . .

DETD . . . for example, woven fabric, nonwoven fabric, net, and sponge, and, furthermore, general-purpose thermoplastic films or thin sheets such as polyethylene **film**, polypropylene **film** and polyester **film**. Among them, the films or thin sheets which are poor in gas permeability may be improved in gas permeability by. . .

DETD . . . retardant, substantially non-combustible inorganic fibers such as metal fibers, ceramic fibers, rock wool fibers, glass fibers, alumina fibers, zirconia fibers, **silicon** nitride fibers, **silicon** carbide fibers, and carbon fibers, and, furthermore, general-purpose fibers containing flame retardants chemically incorporated therein or physically blended therewith. In. . .

DETD . . . may be processed to form uneven surface such as corrugated or baggy surface, the enclosures may be filled in the **dented** portions (protruded downwardly), and another sheet may be placed thereon to bond to each other at the protruded portions. When. . .

DETD . . . method of impregnation and coating, mention may be made of those which use conventional size press, gate roll size press, **film** transfer type size press, roll coater, air doctor coater, rod (bar) coater, blade coater, spray coater and curtain coater.

DETD . . . semiconductor and others with the support-forming component, there may be further used a small amount of at least a self **film**

-forming binder. Examples of the binders used in the present invention are starch, natural gums, chitosan, alginates, cellulose derivatives such as carboxymethyl cellulose and hydroxyethyl cellulose, polyvinyl acetate, polyvinyl **alcohol**, poly-N-vinylpyrrolidone, synthetic resin emulsions such as acrylic emulsion, styrenic emulsion, polyvinyl chloride emulsion and polyvinylidene chloride emulsion, and various latexes. . .

DETD . . . bonded with adhesives to form a composite. Moreover, the photoreactive noxious substance purging material may be put together with a **film** or sheet which does not contain at least the photoreactive semiconductor and which comprises natural fibers such as wood pulp,. . .

DETD . . . powdery photoreactive noxious substance purging agent (A) obtained in Example 1 was put on the nonwoven fabric to fill the **dented** portions with the agent in an amount of 200 g/m.sup.2. This was covered with another nonwoven fabric of 30 g/m.sup.2. . .